



Consommation et
Affaires commerciales Canada
Bureau des brevets
Ottawa, Canada
K1A 0C9

Consumer and
Corporate Affairs Canada
Patent Office

(21) (A1) 2,099,852
(22) 1993/07/05
(43) 1994/01/08

5,070,0/38

(51) INTL.CL. ⁵ B32B-015/08; C23C-014/24; B05D-005/10; B05D-007/02;
B01J-019/08

(19) (CA) APPLICATION FOR CANADIAN PATENT (12)

(54) Process for Utilizing a Metallic Interlayer to Enhance
Adhesion Between a Metal and a Polymeric Substrate

(72) Holmes-Farley, Stephen R. - U.S.A. ;

(71) GTE Products Corporation - U.S.A. ;

(30) (US) 07/909,909 1992/07/07

(57) 17 Claims

Notice: This application is as filed and may therefore contain an
incomplete specification.

Canada

CCA 3254 (10-92) 41 7530-21-936-3254

BEST AVAILABLE COPY

Abstract of the Disclosure

PROCESS FOR UTILIZING A METALLIC INTERLAYER
TO ENHANCE ADHESION BETWEEN A METAL AND
A POLYMERIC SUBSTRATE

5

A process for enhancing adhesion between a metal and a polymeric substrate utilizing a metallic interlayer. In the process, a polymeric substrate is exposed to a plasma at the substrate surface. The pressure is then lowered, and a first metal is vaporized, thereby coating the substrate. While the first metal is vaporizing, a second metal is vaporized and codeposits upon the first metal coated substrate.

10 After a predetermined time, the first metal vaporization is stopped, while the second metal continues to vaporize and deposit upon the substrate.

15

G0311/7034
WRM:PCL:sjd:15010

PROCESS FOR UTILIZING A METALLIC INTERLAYER
TO ENHANCE ADHESION BETWEEN A METAL AND
A POLYMERIC SUBSTRATE

Field of the Invention

The present invention is directed to an improved process for enhancing adhesion between a metal and a 5 polymeric substrate.

Description of the Prior Art

Plastics have replaced more traditional materials, such as glass, in many applications for a variety of 10 reasons including better strength, lighter weight, and lower cost. One such application is in metallization processes, wherein plastics are preferred to glass as a substrate material. Metallized plastics are commonly used as reflectors, primarily in automotive headlamps. 15 A variety of polymeric substrates, including polycarbonate and nylon, are commonly used in the production of lighting reflectors. Although several metals have been applied to these plastics, aluminum is currently used in all automotive headlamp reflectors.

Aluminum is commonly applied to a plasma-treated polymer substrate in a vacuum evaporation process. In the first step, the substrates are put into a vacuum and exposed to a glow discharge. This discharge oxidizes 5 material on the substrate surface and promotes adhesion through a combination of eliminating dirt and other small molecules from the surface, cross-linking the surface, and providing oxygen-containing functional groups with which the subsequently applied aluminum will 10 react. Typically the pressure is then lowered, and the aluminum is evaporated from heated tungsten filaments onto the surface of the substrate to a thickness of approximately 500-1000 angstroms.

Freshly prepared aluminum surfaces have a 15 reflectivity of about 92% over the visible wavelength range. Utilizing a metal having a greater reflectivity would increase the efficiency of a lighting system. For example, silver, one of the best-known reflectors of visible light, which has a reflectivity approaching 98% 20 could theoretically increase the efficiency of a lighting system by approximately 6% without any changes to the lamp itself.

Additionally, silver is less reflective than aluminum in the ultraviolet. For example, at 320 25 nanometers silver reflects less than 10% while aluminum reflects 92%. This lack of reflectivity in the ultraviolet may be potentially useful in preventing degradation of polymeric lenses by ultraviolet radiation.

Silver, however, has several drawbacks, relative to 30 aluminum, for use in lighting systems. These include

higher cost, and lack of environmental resistance of the silver surface. In addition, if silver is substituted for aluminum in the existing process of vacuum evaporation, the adhesion of the silver to the surface of the substrate is not adequate. In many cases the initial adhesion is insufficient, and after exposure, as in several specific environmental tests, adhesion decreases.

In automotive applications these tests are of three types. The first test is immersion in water at an elevated temperature, for example, 96 hours in deionized water at 90°F; the second test is exposure to a salt spray at elevated temperature, for example, 48 hours in 5% NaCl at 100°F; the third test is exposure to humid air, for example, 120 hours in 90% relative humidity at 100°F.

One potential method to enhance adhesion between silver and a polymeric substrate utilizes metallic interlayers, which adhere well to both silver and the substrate. A metal which is known to bond well to both silver and plastics is chromium. For chromium to be effective as an interlayer, however, pressures as low as 1×10^{-7} to 1×10^{-6} mbar are required during the vapor deposition process to prevent the chromium surface from oxidizing before the silver can be deposited. Large scale metal deposition systems, used in the production of automotive headlamps, typically use significantly higher pressures of up to 1×10^{-4} mbar. Operating costs therefore would increase significantly if the lower pressures, required in a

chromium vapor deposition process, are utilized.

It is therefore an object of this invention to provide a process for utilizing a metallic interlayer to enhance adhesion between metals and a polymeric substrate. A further object of the invention is to provide a process for utilizing a metallic interlayer to enhance adhesion between silver and a polymeric substrate at relatively high pressures.

10 Summary of the Invention

According to the present invention, a process to enhance adhesion between a metal and a polymeric substrate utilizes a metallic interlayer.

15 In the process, a polymeric substrate is exposed to a first metal vapor in a reaction chamber, which deposits a first metal coating onto the substrate. A second metal is then vaporized, while the first metal continues to evaporate in the chamber. The first metal coated substrate is then exposed to both metal vapors, 20 which codeposit onto the first metal coated substrate. The vaporization of the first metal is then stopped while the second metal continues to evaporate. The first and second metal coated substrate is then exposed to the second metal vapors, which deposit onto the 25 substrate.

For example, in a preferred embodiment, a polycarbonate substrate is placed into a reaction chamber and exposed to an air plasma. The chamber pressure is then pumped down to about 1×10^{-4} mbar. 30 Chromium is then deposited by vacuum evaporation from a

chromium coated tungsten rod. After a predetermined period of time, silver deposition is then started from a silver filled molybdenum boat. After a predetermined period of codeposition, the chromium evaporation is 5 stopped, while the silver evaporation continues for a predetermined period of time. After the deposition process is completed, greater than 99% of the silver adheres to the polycarbonate substrate during a tape-peel test, performed after exposure to the 10 environment.

Other objects and features of the present invention will become apparent from the following detailed description.

15 Detailed Description of the Invention

The present invention provides a process for enhancing adhesion between a metal and a polymeric substrate utilizing a metallic interlayer at relatively 20 high pressures.

A polymeric substrate is placed into a reaction chamber and exposed to a glow discharge having an energy sufficient to yield a plasma at the substrate surface. The pressure in the chamber is decreased, and a first 25 metal is vaporized. The plasma-treated polymeric substrate is then exposed to the first metal vapor, which deposits a metal coating on the substrate. A second metal is then vaporized with the first metal and, together, both metals are codeposited upon the first 30 metal coated substrate. The first metal vaporization is

then stopped, while the second metal continues to vaporize and deposit upon the first and second metal coated substrate until the desired thickness is achieved.

5 While the process of the present invention may be used to produce various products, of particular interest is the production of automotive headlamp reflectors.

10 Typically, various polymers are used in this application, including polycarbonate and nylon. Most preferably, polycarbonate is used as the polymeric substrate due to its light weight, high impact strength, moldability, and rigidity. It should be noted that almost all plastics, thermoplastics and thermosets, may be utilized in the process of the present invention to produce a variety of metallized products.

15 Once molded into the desired shape, the polymeric substrate is put into a reaction chamber and exposed to a glow discharge having an energy sufficient to yield a plasma. At reduced pressures, glow discharges may be brought about by the use of a high frequency, such as 20 radio or microwave frequency, alternating current passed through a coil surrounding the chamber, or between two external electrodes attached to the chamber. This discharge excites molecules within the chamber which oxidize the substrate surface. Typically, any gas, such 25 as oxygen, nitrogen, or air, may be used within the chamber; in the present embodiment, the air which is present in the chamber oxidizes the substrate surface. The excited molecules on the substrate surface promote adhesion by cleaning the surface, and providing oxygen 30 containing functional groups.

The plasma may alternatively be formed from a corona discharge. A corona discharge may occur at any pressure and in all types of gases. This discharge is physically similar to a glow discharge in a highly non-uniform 5 electric field. The electric energy in a corona discharge is converted chiefly into heat in the gas within the chamber.

After the polymeric substrate is exposed to the plasma treatment, the pressure in the chamber is lowered 10 to about 1×10^{-4} mbar. In the low pressure atmosphere, a first metal is evaporated, and is subsequently deposited on the surface of the substrate. The first metal used in the process of the present invention acts as a metallic interlayer between the 15 polymeric substrate and a second metal. The first metal therefore must adhere well to both the plastic substrate and the second metal. In the production of automotive headlamp reflectors reflectivity is an important feature to be considered when choosing the second metal. 20 Possible metals include copper, aluminum, gold, and silver. Of these, silver, when freshly deposited, is the best reflector of visible light known, and is the most preferred second metal. The first metal, therefore, must adhere well to both the polymeric 25 substrate and silver. Several metals which adhere well to various polymeric substrates as well as other metals include titanium, nickel, palladium, aluminum, and chromium. Of these, chromium is known to bond well to plastics and to form strong bonds with silver, and is 30 therefore the most preferred first metal (metallic

interlayer).

The metal coatings are formed by condensation of metal vapors. Typically, a solid metal holder is positioned on a filament, which is connected to 5 electrodes. A current is passed through the filament to vaporize the metal which is placed in the metal holder. Typically, the metal holder is constructed of a material which has a higher melting point than the metal to be vaporized, and which will not react with the selected 10 metal during the process. These materials preferably include tungsten, molybdenum, tantalum or a ceramic material. In the chamber, the filaments, and therefore the vaporizing metals are typically within three feet of the polymeric substrate material. Most preferably, the 15 vaporizing metals are within two feet of the substrate, due to the nature of the vaporized metal atoms which will deposit upon everything in their path while being transferred from the filaments to the substrate.

In the present process, voltage is applied to the 20 filament holding the first metal, which causes the first metal to evaporate and deposit upon the polymeric substrate. After a predetermined period of time, voltage is applied to a second filament holding the second metal, causing the second metal to evaporate and 25 codeposit with the first metal, upon the first metal coated polymeric substrate. After a predetermined period of codeposition of the two metals, the vaporization of the first metal is stopped, while the second metal continues to deposit upon the substrate for 30 a predetermined period of time. It is noted that the

two filaments are separated by a divider in the chamber to prevent contamination by transfer of particles from one of the metals to the filament holding the other metal.

- 5 A quartz crystal monitor, positioned at the same distance from the vaporizing metals as the substrate, is used to determine the transfer rates of the vaporizing metals. By adjusting the voltage applied to the filaments any desired deposition rates may be achieved.
- 10 The quartz crystal monitor is also used to determine the total amount, or thickness, of the metals deposited on the substrate. In a preferred embodiment of the present process, chromium is deposited on the polymeric substrate at a rate of between about 1 to about 10
- 15 angstroms per second to a total thickness of between about 100 to about 150 angstroms. More preferably, chromium is deposited at about 1 to about 5 angstroms per second; most preferably, about 3 angstroms per second are deposited to a thickness of about 150
- 20 angstroms. Silver deposition preferably occurs at a rate of between about 20 to about 50 angstroms per second; most preferably between about 30 to about 40 angstroms per second. The combined thickness of the codeposited silver and chromium mixture is between about
- 25 100 to about 200 angstroms. The mixture typically comprises between about 2% to about 33% of chromium. Preferably, there is between about 2% to about 14% chromium in the codeposited layer; most preferably, the layer comprises between about 7% to about 9% chromium.
- 30 The codeposition of chromium and silver is critical to

promote adhesion between silver and a polymeric substrate, at the relatively high vacuum evaporation operating pressures of the present invention of about 1×10^{-4} mbar. After a few seconds of codeposition the 5 chromium evaporation is terminated, and the silver continues depositing upon the substrate to a total thickness of between about 500 to about 1000 angstroms. Generally, a thickness of at least 500 angstroms is required to avoid transparency, and provide 10 reflectivity; and, while coating thicknesses may be greater than 1000 angstroms, the level of stress at the surface increases with coating thickness, and cracks may occur in the coating surface.

The deposition rate of silver is greater than the 15 rate for chromium to reduce oxidation before the silver can be deposited. Silver does not adhere as well to oxidized chromium as it does to metallic chromium. Chromium, an oxygen getter metal, will become oxidized more quickly at the relatively high pressures of about 1×10^{-4} mbar used in the present process.

When the quartz crystal monitor determines that the 25 desired metal thicknesses are achieved, the deposition processes of each metal may be stopped by either blocking the path of the metal vapor to the substrate mechanically, or by shutting off the voltage applied to the filaments holding the metals, or by burning out (evaporating) all of the metals.

The present invention will be further illustrated by 30 the following examples which are intended to be illustrative in nature and are not to be construed as

limiting the scope of the invention.

Example I

5 The adhesion of silver to a polycarbonate substrate was compared with the adhesion of aluminum to a polycarbonate substrate, utilizing the known vacuum evaporation process. The experimental results are presented in Table 1.

10 The first samples were not cleaned prior to testing; the second samples were cleaned by scrubbing with soap and water, and then dried prior to testing; and the third samples were similarly cleaned, and subjected to an air plasma (to simulate the glow discharge used in
15 the commercial process). The adhesion was tested first, initially after the vacuum evaporation process, and second, after water immersion for 18 hours at 25°C. A "Pass" means that when adhesive tape (Permanent Mending Tape, 3M Corporation, St. Paul, MN) is applied to the
20 metallized substrate, which has been scored with a razor blade into a 1 centimeter square grid, and then peeled up, less than 1% of the silver peels off the surface with the tape. The percentage indicated in failed samples is that portion of the silver that peels up.

TABLE IA. Silver Adhesion

<u>Sample</u>	<u>Substrate</u>	<u>Initial Adhesion</u>	<u>After Water Immersion (18h, 25°C)</u>
1.	Polycarbonate	Fail (80%)	Fail (80%)
2.	Polycarbonate (Cleaned)	Fail (70%)	Fail (90%)
3.	Polycarbonate (Cleaned then Air Plasma)	Fail (90%)	Fail (100%)

B. Aluminum Adhesion

<u>Sample</u>	<u>Substrate</u>	<u>Initial Adhesion</u>	<u>After Water Immersion (18h, 25°C)</u>
1.	Polycarbonate	Pass	Fail (100%)
2.	Polycarbonate	Pass	Fail (100%)
3.	Polycarbonate (Cleaned then Air Plasma)	Pass	Pass

This experiment shows that when silver is substituted for aluminum in a standard vacuum evaporation process, adhesion is not adequate initially and is less adequate after water immersion. It is also noted that aluminum adhesion is promoted by utilizing the air plasma prior to the vacuum evacuation process.

5

Example II

The use of a metallic interlayer to enhance adhesion between silver and a polymeric substrate was examined. Chromium was chosen as the metallic interlayer to enhance adhesion between polycarbonate and silver.

5 The experimental results are presented in Table 2.

In the polycarbonate-chromium-silver structure, a chromium layer having a thickness of between 100 to about 200 angstroms was deposited to a polycarbonate substrate in a vacuum evaporation process. A silver 10 layer of about 500 angstroms thickness was then deposited in a second vacuum evaporation process. The two deposition processes were run at various pressures, with and without exposure to a brief air plasma prior to the chromium deposition process, to determine the most 15 effective pressures for the deposition processes as well as to determine if there is any advantage to applying a plasma to the surface of the polymeric substrate.

The adhesion of the silver layer was tested initially after the vacuum evaporation process. A 20 "Pass" means that when adhesive tape (Permanent Mending Tape, 3M Corporation, St. Paul, MN) is applied to the metallized substrate, which has been scored with a razor blade into a 1 centimeter square grid, and then peeled up, less than 1% of the silver peels off the chromium 25 layer with the tape. The percentage indicated in failed samples is that portion of the silver that peels up.

TABLE 2

<u>Sample</u>	<u>Plasma</u>	<u>Pressure</u> 1×10^{-4} mbar	<u>Chromium</u> 150ang.	<u>Silver</u> <u>Adhesion</u>
1	No	1×10^{-4}	150	Fail, 100%
2	No	4×10^{-5}	150	Fail, 100%
3	No	2×10^{-5}	100	Fail, 20-100%
4	No	1.5×10^{-5}	100	Fail, 10%
5	No	5×10^{-6}	160	PASS
6	No	5×10^{-7}	120	PASS
7	Yes	1×10^{-4}	150	Fail, 100%
8	Yes	4×10^{-5}	150	Fail, 100%
9	Yes	2×10^{-5}	100	Fail, 20-100%
10	Yes	2×10^{-6}	100	Fail, 2-5%
11	Yes	5×10^{-7}	120	PASS

This experiment illustrates that chromium may be used as an effective adhesion promoting interlayer. However, chromium is only effective when it is deposited at relatively low pressures of between 5×10^{-6} to 5×10^{-7} mbar (samples 5, 6 and 11). Chromium oxidized more quickly at the relatively high pressures of samples 1-4 and 7-10, which inhibited silver adhesion.

The application of a plasma to the surface of the polymeric substrate prior to depositing the chromium layer did not appear to significantly effect silver

adhesion.

Example III

5 The use of a chromium interlayer to enhance adhesion
between silver and a polycarbonate substrate at
relatively high pressures of about 1×10^{-4} mbar was
examined.

10 A polycarbonate sheet was washed in soap and water,
followed by a rinsing in deionized water. The sheet was
then placed in a reaction chamber, and the chamber was
pumped down to about 1×10^{-5} mbar. Air was then
leaked into the chamber to set up a dynamic pressure of
 1×10^{-4} mbar. Chromium was then deposited by vacuum
15 evaporation, from a chromium coated tungsten rod, at
about 3 angstroms per second to a thickness of about 150
angstroms. Silver deposition by vacuum evaporation was
then started, from a silver filled molybdenum boat, at
about 34 angstroms per second. After about 5 seconds of
20 codeposition the chromium evaporation was terminated, as
the silver continued to deposit until a total thickness
of 850 angstroms was reached (approximately 150
angstroms of pure chromium, 185 angstroms of mixed
silver and chromium, and about 515 angstroms of pure
25 silver).

During this deposition the pressure dropped slightly
due to the gettering action of the freshly deposition
chromium, with the pressure remaining approximately
between $5 - 8 \times 10^{-5}$ mbar throughout the process.

30 The sample was then removed from the chamber and

scored with a razor blade into a 1 centimeter square grid. Adhesive tape was applied by hand and peeled up. None of the metal coating released from the plastic substrate. A second sheet, coated in a similar manner, 5 was exposed to water at 90°F for 96 hours, dried and tested for adhesion in the same manner. In this test 30% of the silver coating released from the plastic substrate.

10 Example IV

Example III was repeated identically except that the polycarbonate sheet was exposed to an air plasma for 60 seconds at 0.4 mbar at the high setting of a Harrick 15 Model PDC-23G plasma cleaner prior to insertion into the reaction chamber. On removal from the chamber, the sample was scored and tested with tape as in Example III. None of the metal coating released from the plastic substrate. A second sheet coated in a similar 20 manner, was exposed to water at 90°F for 96 hours, dried and tested for adhesion in the same manner. In this test none of the metal coating released from the plastic substrate. This example demonstrates the usefulness of an air plasma treatment on the substrate prior to 25 deposition of the chromium and silver.

Example V

A polycarbonate sheet was washed in soap and water, 30 followed by a rinsing in deionized water. The sheet was

placed into a reaction chamber and the chamber was pumped down to 1×10^{-5} mbar. Air was then leaked into the chamber to set up a dynamic pressure of 1×10^{-4} mbar. Chromium was then deposited by vacuum evaporation, from a chromium coated tungsten rod at about 3 angstroms per second to a thickness of about 150 angstroms. Chromium deposition was terminated, and 10 seconds later silver deposition was started from a silver filled molybdenum boat at about 34 angstroms per second, to a total thickness of 905 angstroms (approximately 150 angstroms of pure chromium and 755 angstroms of pure silver). During this deposition the pressure dropped slightly due to the gettering action of the freshly deposited chromium, with the pressure remaining approximately between $7 - 10 \times 10^{-5}$ mbar throughout the process.

The sample was then removed from the chamber and scored with a razor blade into a 1 centimeter square grid. Adhesive tape was applied by hand and then peeled up. All of the silver coating released from the chromium coated plastic substrate. This example demonstrates that the codeposition process is critical to promote adhesion between silver and a polymeric substrate.

25

Example VI

Example V was repeated identically except that the polycarbonate sheet was exposed to an air plasma for 60 seconds at 0.4 mbar at the high setting of a plasma

cleaner prior to insertion into a reaction chamber. On removal from the chamber the sample was scored and tested with tape as in Example V. All of the silver coating released from the chromium coated substrate.

5 This example further demonstrates that the codeposition process is critical to promote adhesion between silver and a polymeric substrate.

Although particular embodiments of the invention have been described in detail for purposes of 10 illustration, various modifications may be made without departing from the spirit and scope of the invention. Accordingly, the invention is not to be limited except as by the appended claims.

CLAIMS

What is claimed is:

1. A process comprising:
depositing a first metal coating onto a polymeric substrate;
codepositing a second metal and said first metal
coating onto said first metal coated substrate; and
depositing said second metal onto said first and
second metal coated substrate.
- 5 2. The process as claimed in claim 1 wherein greater
than 99% of said second metal coating adheres to said
substrate when the second metal coating is subjected to
a tape peel test.
3. The process as claimed in claim 1 wherein said
polymeric substrate is selected from the group
consisting of polycarbonate and nylon.
4. The process as claimed in claim 1 wherein said
polymeric substrate is polycarbonate.
5. The process as claimed in claim 1 wherein said
polymeric substrate is nylon.
6. The process as claimed in claim 1 wherein said first
metal is chromium.

7. The process as claimed in claim 1 wherein said first metal is aluminum

8. The process as claimed in claim 1 wherein said second metal is silver.

9. The process as claimed in claim 1 wherein said polymeric substrate is exposed to a glow discharge having an energy sufficient to yield a plasma at the substrate surface, prior to depositing said first metal.

10. The process as claimed in claim 1 wherein said first and second metals are deposited by vacuum evaporation at a pressure of about 1×10^{-4} mbar.

11. A process comprising:

depositing a chromium coating onto a polycarbonate substrate;

5 codepositing a silver and chromium coating onto said chromium coated substrate; and

depositing said silver onto said chromium and silver coated substrate.

12. The process as claimed in claim 11 wherein greater than 99% of said silver coating adheres to said substrate when the silver coating is subjected to a tape peel test.

13. The process as claimed in claim 11 wherein said

polycarbonate substrate is exposed to a glow discharge having an energy sufficient to yield a plasma at the substrate surface, prior to depositing said chromium.

14. The process as claimed in claim 11 wherein said chromium and said silver are deposited by vacuum evaporation at a pressure of about 1×10^{-4} mbar.

15. An article comprising a polymeric substrate, a silver layer on said polymeric substrate and a metallic interlayer between said silver layer and said polymeric substrate; wherein said metallic interlayer comprises a 5 chromium layer adhered to said substrate, and a chromium and silver codeposited layer between said chromium layer and said silver layer; and wherein said substrate is selected from the group consisting of polycarbonate and 10 nylon.

16. The silver coated polymeric substrate as claimed in claim 15 wherein said chromium and silver codeposited layer comprises between about 2% to about 33% chromium.

17. Each and every novel feature or novel combination of features herein disclosed.

R. WILLIAM WRAY & ASSOCIATES
BOX 2760 - STATION D
OTTAWA, CANADA K1P 5W8
PATENT AGENT FOR THE APPLICANT

SUBSTITUTE
REPLACEMENT

SECTION is not Present

Cette Section est Absente

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.